

# PATENT ABSTRACTS OF JAPAN

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(21)Application number : **08-357964** (71)Applicant : **SANYO ELECTRIC CO LTD**

(22)Date of filing : **27.12.1996** (72)Inventor : **WATANABE HIROSHI  
FUJIMOTO HIROYUKI  
SUNAKAWA TAKUYA  
NOMA TOSHIYUKI  
NISHIO KOJI**

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## **(54) LITHIUM SECONDARY BATTERY**

### **(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide a lithium secondary battery, in which a compound oxide is hard to be deteriorated and which has remarkably excellent charge and discharge cycle characteristics, by using a compound oxide of Li and transition element such as Co, Ni, Mn as a positive electrode active material, and regulating the atomic ratio of Li to the transition element on the surface and inside of particles of the compound oxide.

**SOLUTION:** A compound oxide of Li and one or more kinds of transition element such as Co, Ni, Mn, Ti, V, Cr, Fe, Sn and Zn is used as a positive electrode active material so as to form a lithium secondary battery. In this case, in the compound oxide, the atomic ratios of Li to the transition element on the surface and inside the particles are set at 0.9-1.2, and the former atomic ratio is set larger than the latter atomic ratio. As the compound oxide,  $\text{Li}_{\alpha}\text{Co}_{1-x-y}\text{Ni}_x\text{Mn}_y\text{O}_2$  ( $0.9 \leq \alpha \leq 1.2$ ,  $x \geq 0$ ,  $y \geq 0$ ,  $0 \leq x+y \leq 1$ ) is preferable.

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## CLAIMS

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### [Claim(s)]

[Claim 1] The lithium secondary battery which each of lithiums on the front face of a particle of said multiple oxide, atomic ratios of a transition element, and the lithiums inside a particle and the atomic ratios of a transition element are 0.9-1.2, and is characterized by the former atomic ratio being larger than the latter atomic ratio in the lithium secondary battery which uses as positive active material a multiple oxide with at least one sort of transition elements chosen from the group which consists of a lithium, cobalt and nickel, manganese, titanium, vanadium, chromium, iron, copper, and zinc.

[Claim 2] The lithium secondary battery according to claim 1 said whose multiple oxide is a multiple oxide of a lithium and at least one sort of transition elements chosen from the group which it becomes from cobalt, nickel, and manganese.

[Claim 3] The lithium secondary battery according to claim 1 said whose multiple oxide is  $\text{Li}_{a} \text{Co}_{1-x-y} \text{Ni}_x \text{Mn}_y \text{O}_2$  (however,  $0.9 \leq a \leq 1.2$ ,  $x \geq 0$ ,  $y \geq 0$ ,  $0 \leq x+y \leq 1$ ).

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[The technical field to which invention belongs] This invention relates to amelioration of the multiple oxide aiming at improving the charge-and-discharge cycle property of this kind of cell in detail with respect to the lithium secondary battery which uses as positive active material a multiple oxide with at least one sort of transition elements chosen from the group which consists of a lithium, cobalt and nickel, manganese, titanium, vanadium, chromium, iron, copper, and zinc.

#### [0002]

[Description of the Prior Art] since a lithium secondary battery does not need to take the decomposition voltage of water into consideration in recent years unlike the alkaline cell which uses an alkali water solution as the electrolytic solution, a high-tension design is possible by selecting positive active material suitably -- etc. -- it is observed from the reason.

[0003] \*\*(ing) -- as the positive active material of a lithium secondary battery --  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  etc. -- the multiple oxide of 1:1 is well known for the atomic ratio of a lithium and a transition element.

[0004] However, there is a problem that a charge-and-discharge cycle property is not good in the lithium secondary battery which used this kind of multiple oxide. It is because this kind of multiple oxide reacts with the electrolytic solution, or the crystal structure changes with the repeats of charge and discharge and it is easy to deteriorate.

[0005]  $\text{LiCoO}_2$  As a multiple oxide which has improved the charge-and-discharge cycle property,  $\text{Li}_x \text{CoO}_2$  ( $1.05 \leq x \leq 1.3$ ) is proposed (refer to JP,3-127454,A). Stabilization of the crystal structure is attained by making the atomic ratio (Li atom / Co atom) of a lithium and cobalt larger than 1.

[0006] However, even if it used  $\text{Li}_x \text{CoO}_2$  ( $1.05 \leq x \leq 1.3$ ) as positive active material as

a result of this invention persons' examination, it turned out that the lithium secondary battery which was extremely excellent in the charge-and-discharge cycle property is not obtained.

[0007] Therefore, this invention aims at offering the lithium secondary battery which was extremely excellent in the charge-and-discharge cycle property.

[0008]

[Means for Solving the Problem] The lithium secondary battery (the "this invention cell" is called hereafter) concerning this invention In the lithium secondary battery which uses as positive active material a multiple oxide with at least one sort of transition elements chosen from the group which consists of a lithium, cobalt and nickel, manganese, titanium, vanadium, chromium, iron, copper, and zinc Each of lithiums on the front face of a particle of said multiple oxide, atomic ratios of a transition element, and the lithiums inside a particle and the atomic ratios of a transition element are 0.9-1.2, and the former atomic ratio is characterized by being larger than the latter atomic ratio. In addition, in this description, a lithium and the atomic ratio of a transition element say the value (Li atom / transition element atom) of the ratio of a lithium atom and a transition element atom.

[0009] As the above-mentioned multiple oxide, a multiple oxide with at least one sort of transition elements chosen from the lithium and the group which consists of cobalt, nickel, and manganese expressed with empirical formula  $\text{Li}_a \text{Co}_{1-x-y} \text{Ni}_x \text{Mn}_y \text{O}_2$  (however,  $0.9 \leq a \leq 1.2$ ,  $x \geq 0$ ,  $y \geq 0$ ,  $0 \leq x+y \leq 1$ ) is illustrated.

[0010] Each of lithiums on the front face of a particle, atomic ratios of a transition element, and the lithiums inside a particle and the atomic ratios of a transition element are regulated by 0.9-1.2. When these atomic ratios are less than 0.9, capacity decreases. On the other hand, when 1.2 is exceeded, since a superfluous lithium generates a segregation phase and the crystal structure becomes an ununiformity, a charge-and-discharge cycle property falls.

[0011] In order to improve the charge-and-discharge cycle property of the lithium secondary battery which uses the multiple oxide of a lithium and a transition element as positive active material, the lithium on the front face of a particle and the atomic ratio of a transition element have the description of this invention in the point which used the larger multiple oxide than the lithium inside a particle, and the atomic ratio of a transition element as positive active material. So, it is possible to use the various ingredients which especially a limit does not have about other ingredients which constitute cells, such as a negative-electrode ingredient and the electrolytic solution, and are conventionally used as an object for lithium secondary batteries, or are proposed.

[0012] As the electrolytic solution, ethylene carbonate, propylene carbonate, Butylene carbonate, dimethyl carbonate, ethyl methyl carbonate, To diethyl carbonate, sulfolane, 1, 2-dimethoxyethane, tetrahydrofuran and 1, and 3-dioxolanes or two or more sorts of these mixed solvents They are  $\text{LiCF}_3 \text{SO}_3$ ,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , and  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$  as an electrolyte salt. Or  $\text{LiCF}_3 \text{SO}_3$  The melted solution is illustrated.

[0013] As a negative-electrode ingredient, carbon materials, such as lithium alloy [, such as a metal lithium; lithium-aluminium alloy, ]; and a graphite, and corks, are illustrated.

[0014] The reason like \*\*\*\* this invention cell of a configuration is excellent in a charge-and-discharge cycle property is guessed as following, although it is not certain.

[0015] Although it tends to be thought that the stability of the crystal structure at the time of charge and discharge is with a particle front face and the interior of a particle, and is equal when the lithium inside a particle, the atomic ratio of a transition element, and the lithium on the front face of a particle and the atomic ratio of a transition element are the same multiple oxides (i.e., when the whole particle is the multiple oxide of a uniform presentation), the particle front face which touches the electrolytic solution is high activity (instability) chemically actually compared with the interior of a particle. On a particle front face, it will be firmly restricted during a crystal by especially the lithium ion ( $\text{Li}^+$ ) that comes and goes between a multiple oxide and the electrolytic solutions at the time of charge and discharge, and it will be in an unstable condition chemically by a solvation etc. compared with the interior of a particle. Such a particle front face reacts with the electrolytic solution chemically, or the crystal structure changes with the repeats of charge and discharge, and an unstable multiple oxide tends to deteriorate.

[0016] On the other hand, as for the case of a lithium and a transition element multiple oxide with larger lithium on the front face of a particle and atomic ratio of a transition element than the lithium inside a particle, and the atomic ratio of a transition element, the direction of a particle front face tends to stabilize a lithium ion compared with the interior of a particle. For this reason, since it is drawn on a particle front face by the lithium ion inside a particle and a particle front face is stable, it is hard to deteriorate.

[0017] However, if there is an excessive difference in the lithium inside a particle, the atomic ratio of a transition element, the lithium on the front face of a particle, and the atomic ratio of a transition element, in order for the continuity of the crystal structure a particle front face and inside a particle to fall, a particle front face stops being able to draw the lithium ion inside a particle easily, and stabilization on the front face of a particle is checked. Each of lithiums on the front face of a particle, atomic ratios of a transition element, and the lithiums inside a particle and the atomic ratios of a transition element of the multiple oxide in this invention are 0.9-1.2, and the difference of an atomic ratio seems not to say at the maximum that stabilization on the front face of a particle is checked with 0.3 since it is small, and the difference of an atomic ratio is excessive.

[0018]

[Example] It is possible to change this invention suitably in the range which is not limited to the following example at all and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0019] (Experiment 1) In this experiment, it investigated about the effectiveness at the time of applying this invention to the lithium secondary battery which uses the multiple oxide of a lithium and cobalt as positive active material.

[0020] It mixes with a lithium by the atomic ratio 1:1 of cobalt, a lithium carbonate and cobalt hydroxide are heat-treated by 850-degreeC in air for 20 hours, an Ishikawa style stone mill mortar grinds, and it is  $\text{LiCoO}_2$  with a mean particle diameter of 5 micrometers. It obtained. Moreover, it mixes with a lithium by the atomic ratio 1.1:1 of cobalt, a lithium carbonate and cobalt hydroxide are heat-treated by 850-degreeC in air for 20 hours, an Ishikawa style stone mill mortar grinds, and it is  $\text{Li}_{1.1}\text{CoO}_2$  with a mean particle diameter of 1 micrometer. It obtained. subsequently,  $\text{LiCoO}_2$   $\text{Li}_{1.1}\text{CoO}_2$  the weight ratio 9:1 -- enough -- mixing -- the inside of air -- 700-degreeC -- 10 hours -- heat-treating -- a particle front face --  $\text{Li}_{1.1}\text{CoO}_2$  from -- becoming -- the interior of a

particle -- LiCoO<sub>2</sub> from -- the multiple oxide of the becoming lithium and cobalt was obtained. this multiple oxide, the acetylene black as an electric conduction agent, and the polyvinylidene fluoride as a binder -- the weight ratio 90:6:4 -- mixing -- a positive electrode -- a mixture -- preparing -- this positive electrode -- a mixture -- moulding pressure 2 t/cm<sup>2</sup> Pressing was carried out to discoid with a diameter of 20mm, it heat-treated by 250-degreeC for 2 hours, and the positive electrode was produced.

[0021] The rolled plate of a metal lithium was pierced to discoid with a diameter of 20mm, and the negative electrode was produced.

[0022] LiClO<sub>4</sub> [ one mol / / ] (lithium perchlorate) was melted 1. to the mixed solvent of the volume ratio 1:1 of propylene carbonate and 1 and 2-dimethoxyethane, and the electrolytic solution was prepared to it.

[0023] The lithium secondary battery (this invention cell) A1 of a flat form was produced using a positive electrode, an above-mentioned negative electrode, and the above-mentioned electrolytic solution (cell dimension:; with an outer diameter of 20.0mm thickness of 2.5mm). The porous membrane made from polypropylene was used for the separator.

[0024] Furthermore, the various multiple oxides shown in a table 1 were prepared like the point, these were used as positive active material, and this invention cells A2-A6 and the comparison cells B1-B11 were produced. Each used multiple oxide mixes, heat-treats and produces the multiple oxide of the lithium of 5 micrometers of mean diameters and cobalt which should constitute the interior of a particle, and the multiple oxide of the lithium of 1 micrometer of mean diameters and cobalt which should constitute a particle front face by the weight ratio 9:1. In addition, the multiple oxide of the same presentation also mixes the multiple oxide of the lithium of these two presentations and cobalt with which mean diameters differ, and a particle front face and the interior of a particle heat-treat it, and produce.

[0025] About above-mentioned this invention cells A1-A6 and comparison cells B1-B11, after charging to 4.3V by 3mA, the charge-and-discharge cycle trial which makes 1 cycle the process which discharges to 3V by 3mA was performed, and the charge-and-discharge cycle life and the maximum discharge capacity of each cell were calculated. It was estimated that a charge-and-discharge cycle life was also at the number of charge-and-discharge cycles until discharge capacity falls to 80% of the maximum discharge capacity. A result is shown in a table 1.

[0026]

[A table 1]

電池	Li と Co の原子比		充放電サイクル 寿命(回)	最大放電容量 (mA h/g)
	粒子内部	粒子表面		
A 1	1. 0	1. 1	1 5 1	1 3 6
A 2	1. 0	1. 2	1 5 3	1 3 5
A 3	0. 9	1. 0	1 5 2	1 3 2
A 4	0. 9	1. 1	1 5 2	1 3 2
A 5	0. 9	1. 2	1 5 2	1 3 3
A 6	1. 1	1. 2	1 5 1	1 3 4
B 1	0. 8	0. 8	8 5	1 1 7
B 2	0. 9	0. 9	1 2 5	1 3 0
B 3	1. 0	1. 0	1 3 6	1 3 6
B 4	1. 1	1. 1	1 3 8	1 3 7
B 5	1. 2	1. 2	1 3 5	1 3 7
B 6	1. 3	1. 3	1 3 5	1 3 8
B 7	1. 0	0. 8	1 3 2	1 3 5
B 8	1. 0	1. 3	1 3 3	1 3 6
B 9	1. 2	0. 9	1 3 5	1 3 7
B 10	1. 2	1. 0	1 3 6	1 3 6
B 11	1. 2	1. 1	1 3 5	1 3 7

[0027] As shown in a table 1, this invention cells A1-A6 have a long charge-and-discharge cycle life compared with the comparison cells B1-B11. This data shows that the lithium secondary battery the lithium on the front face of a particle and the atomic ratio of cobalt excelled [ lithium secondary battery ] in the charge-and-discharge cycle property extremely by using the multiple oxide of the lithium inside a particle, a larger lithium than the atomic ratio of cobalt, and cobalt as positive active material is obtained.

[0028] (Experiment 2) In this experiment, it investigated about the effectiveness at the time of applying this invention to the lithium secondary battery which uses the multiple oxide of a lithium and nickel as positive active material.

[0029] It replaced with cobalt hydroxide and nickel hydroxide was used, and except having heat-treated in the oxygen ambient atmosphere, like the experiment 1, the multiple oxide of a mutually different lithium and nickel was produced, and the presentation inside the particle front face shown in a table 2 and/or a particle used each of these multiple oxides as positive active material, and produced this invention cells A7-A12 and the comparison cells B12-B22. Subsequently, the charge-and-discharge cycle trial of the conditions same about each cell as experiment 1 was performed, and the charge-and-discharge cycle life and the maximum discharge capacity of each cell were calculated. A result is shown in a table 2.

[0030]

[A table 2]

[0031] As shown in a table 2, this invention cells A7-A12 have a long charge-and-discharge cycle life compared with the comparison cells B12-B22. This data shows that the lithium secondary battery the lithium on the front face of a particle and the atomic ratio of nickel excelled [ lithium secondary battery ] in the charge-and-discharge cycle property extremely by using the multiple oxide of the lithium inside a particle, a larger lithium than the atomic ratio of nickel, and nickel as positive active material is obtained.

[0032] (Experiment 3) In this experiment, it investigated about the effectiveness at the time of applying this invention to the lithium secondary battery which uses the multiple oxide of a lithium, cobalt, and nickel as positive active material.

[0033] As multiple oxide synthetic powder, like the experiment 1, the multiple oxide of a lithium, mutually different cobalt, and mutually different nickel was produced, and the presentation inside the particle front face shown in a table 3 and/or a particle used each of these multiple oxides as positive active material, and produced this invention cells A13-A18 and the comparison cells B23-B33 except having used a lithium carbonate, cobalt hydroxide, and nickel hydroxide. In addition, all the mixed mole ratios of the cobalt hydroxide at the time of producing a multiple oxide and nickel hydroxide were set to 9:1. Subsequently, the charge-and-discharge cycle trial of the conditions same about each cell as experiment 1 was performed, and the charge-and-discharge cycle life and the maximum discharge capacity of each cell were calculated. A result is shown in a table 3.

[0034]

[A table 3]

[0035] As shown in a table 3, this invention cells A13-A18 have a long charge-and-discharge cycle life compared with the comparison cells B23-B33. This data shows that the lithium secondary battery the atomic ratio with the lithium on the front face of a particle, cobalt, and nickel excelled [ lithium secondary battery ] in the charge-and-discharge cycle property extremely by using the multiple oxide of the lithium inside a particle, cobalt and a larger lithium and cobalt than an atomic ratio with nickel, and nickel as positive active material is obtained.

[0036] (Experiment 4) In this experiment, it investigated about the effectiveness at the time of applying this invention to the lithium secondary battery which uses the multiple oxide of a lithium, cobalt, nickel, and manganese as positive active material.

[0037] As multiple oxide synthetic powder, a lithium carbonate, cobalt hydroxide, nickel hydroxide, and a manganese dioxide are used, and it is made to be the same as that of experiment 1 except having heat-treated in the oxygen ambient atmosphere, The multiple oxide of a lithium, cobalt, mutually different nickel, and mutually different manganese was produced, and the presentation inside the particle front face shown in a table 4 and/or a particle used each of these multiple oxides as positive active material, and produced this invention cells A19-A24 and the comparison cells B34-B44. In addition, all the mixed mole ratios of the cobalt hydroxide at the time of producing a multiple oxide, nickel hydroxide, and a manganese dioxide were set to 1:7:2. Subsequently, the charge-and-discharge cycle trial of the conditions same about each cell as experiment 1 was performed, and the charge-and-discharge cycle life and the maximum discharge capacity of each cell were calculated. A result is shown in a table 4.

[0038]

[A table 4]

電池	Li と、Co、Ni 及び Mn との原子比		充放電サイクル 寿命 (回)	最大放電容量 (mA h/g)
	粒子内部	粒子表面		
A 19	1. 0	1. 1	1 4 5	1 8 1
A 20	1. 0	1. 2	1 4 7	1 8 2
A 21	0. 9	1. 0	1 4 4	1 7 9
A 22	0. 9	1. 1	1 4 5	1 8 0
A 23	0. 9	1. 2	1 4 5	1 8 0
A 24	1. 1	1. 2	1 4 5	1 8 1
B 34	0. 8	0. 8	6 7	1 6 3
B 35	0. 9	0. 9	1 2 4	1 8 0
B 36	1. 0	1. 0	1 2 7	1 8 2
B 37	1. 1	1. 1	1 3 3	1 8 2
B 38	1. 2	1. 2	1 3 6	1 8 4
B 39	1. 3	1. 3	1 3 2	1 8 4
B 40	1. 0	0. 8	1 3 0	1 8 1
B 41	1. 0	1. 3	1 2 9	1 8 2
B 42	1. 2	0. 9	1 3 2	1 8 2
B 43	1. 2	1. 0	1 3 3	1 8 3
B 44	1. 2	1. 1	1 3 2	1 8 3

[0039] As shown in a table 4, this invention cells A19-A24 have a long charge-and-discharge cycle life compared with the comparison cells B34-B44. This data shows that the lithium secondary battery the atomic ratio with the lithium on the front face of a particle, cobalt, nickel, and manganese excelled [ lithium secondary battery ] in the charge-and-discharge cycle property extremely by using the multiple oxide of the lithium inside a particle, cobalt, nickel and a larger lithium and cobalt than an atomic ratio with manganese, and nickel, and manganese as positive active material is obtained.

[0040] Although that to which a particle front face and the interior of a particle mixed, heat-treated and produced the multiple oxide powder of this presentation which is two with which mean particle diameter differs as a multiple oxide of the same presentation was used in the above-mentioned experiments 1-4, also when mean particle diameter used the multiple oxide powder which is 5 micrometers as it was, it checked separately that the almost same result was obtained.

[0041] Although investigated in the above-mentioned experiments 1-4 about the effectiveness at the time of applying a multiple oxide with at least one sort of transition elements chosen from the group which consists this invention of a lithium, cobalt and nickel, and manganese to the lithium secondary battery used as positive active material Also about the lithium secondary battery which used other multiple oxides specified by this invention Each of lithiums on the front face of a particle of a multiple oxide, atomic ratios of a transition element, and the lithiums inside a particle and the atomic ratios of a transition element are set to 0.9-1.2, and the former atomic ratio is made larger than the latter atomic ratio. It checked separately that the lithium secondary battery which was extremely excellent in the charge-and-discharge cycle property was obtained.

[0042]  
[Effect of the Invention] According to this invention, the lithium secondary battery which was extremely excellent in the charge-and-discharge cycle property is offered.

## TECHNICAL FIELD

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[The technical field to which invention belongs] This invention relates to amelioration of the multiple oxide aiming at improving the charge-and-discharge cycle property of this kind of cell in detail with respect to the lithium secondary battery which uses as positive active material a multiple oxide with at least one sort of transition elements chosen from the group which consists of a lithium, cobalt and nickel, manganese, titanium, vanadium, chromium, iron, copper, and zinc.

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## EFFECT OF THE INVENTION

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[Effect of the Invention] According to this invention, the lithium secondary battery which was extremely excellent in the charge-and-discharge cycle property is offered.

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## TECHNICAL PROBLEM

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[Description of the Prior Art] since a lithium secondary battery does not need to take the decomposition voltage of water into consideration in recent years unlike the alkaline cell which uses an alkali water solution as the electrolytic solution, a high-tension design is possible by selecting positive active material suitably -- etc. -- it is observed from the reason.

[0003] \*\*(ing) -- as the positive active material of a lithium secondary battery --  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  etc. -- the multiple oxide of 1:1 is well known for the atomic ratio of a lithium and a transition element.

[0004] However, there is a problem that a charge-and-discharge cycle property is not good in the lithium secondary battery which used this kind of multiple oxide. It is because this kind of multiple oxide reacts with the electrolytic solution, or the crystal structure changes with the repeats of charge and discharge and it is easy to deteriorate.

[0005]  $\text{LiCoO}_2$  As a multiple oxide which has improved the charge-and-discharge cycle property,  $\text{Li}_x \text{CoO}_2$  ( $1.05 \leq x \leq 1.3$ ) is proposed (refer to JP,3-127454,A). Stabilization of the crystal structure is attained by making the atomic ratio (Li atom / Co atom) of a lithium and cobalt larger than 1.

[0006] However, even if it used  $\text{Li}_x \text{CoO}_2$  ( $1.05 \leq x \leq 1.3$ ) as positive active material as a result of this invention persons' examination, it turned out that the lithium secondary battery which was extremely excellent in the charge-and-discharge cycle property is not obtained.

[0007] Therefore, this invention aims at offering the lithium secondary battery which was extremely excellent in the charge-and-discharge cycle property.

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## MEANS

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[Means for Solving the Problem] The lithium secondary battery (the "this invention cell" is called hereafter) concerning this invention In the lithium secondary battery which uses as positive active material a multiple oxide with at least one sort of transition elements chosen from the group which consists of a lithium, cobalt and nickel, manganese, titanium, vanadium, chromium, iron, copper, and zinc Each of lithiums on the front face of a particle of said multiple oxide, atomic ratios of a transition element, and the lithiums inside a particle and the atomic ratios of a transition element are 0.9-1.2, and the former atomic ratio is characterized by being larger than the latter atomic ratio. In addition, in this description, a lithium and the atomic ratio of a transition element say the value (Li atom / transition element atom) of the ratio of a lithium atom and a transition element atom.

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[0015] Although it tends to be thought that the stability of the crystal structure at the time of charge and discharge is with a particle front face and the interior of a particle, and is equal when the lithium inside a particle, the atomic ratio of a transition element, and the lithium on the front face of a particle and the atomic ratio of a transition element are the same multiple oxides (i.e., when the whole particle is the multiple oxide of a uniform presentation), the particle front face which touches the electrolytic solution is high activity (instability) chemically actually compared with the interior of a particle. On a particle front face, it will be firmly restricted during a crystal by especially the lithium ion ( $Li^+$ ) that comes and goes between a multiple oxide and the electrolytic solutions at the time of charge and discharge, and it will be in an unstable condition chemically by a solvation etc. compared with the interior of a particle. Such a particle front face reacts with the electrolytic solution chemically, or the crystal structure changes with the repeats of charge and discharge, and an unstable multiple oxide tends to deteriorate.

[0016] On the other hand, as for the case of a lithium and a transition element multiple oxide with larger lithium on the front face of a particle and atomic ratio of a transition element than the lithium inside a particle, and the atomic ratio of a transition element, the direction of a particle front face tends to stabilize a lithium ion compared with the interior of a particle. For this reason, since it is drawn on a particle front face by the lithium ion inside a particle and a particle front face is stable, it is hard to deteriorate.

[0017] However, if there is an excessive difference in the lithium inside a particle, the atomic ratio of a transition element, the lithium on the front face of a particle, and the atomic ratio of a transition element, in order for the continuity of the crystal structure a particle front face and inside a particle to fall, a particle front face stops being able to draw the lithium ion inside a particle easily, and stabilization on the front face of a particle is checked. Each of lithiums on the front face of a particle, atomic ratios of a transition element, and the lithiums inside a particle and the atomic ratios of a transition element of the multiple oxide in this invention are 0.9-1.2, and the difference of an atomic ratio seems not to say at the maximum that stabilization on the front face of a particle is checked with 0.3 since it is small, and the difference of an atomic ratio is excessive.

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## EXAMPLE

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[Example] It is possible to change this invention suitably in the range which is not limited to the following example at all and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0019] (Experiment 1) In this experiment, it investigated about the effectiveness at the time of applying this invention to the lithium secondary battery which uses the multiple oxide of a lithium and cobalt as positive active material.

[0020] It mixes with a lithium by the atomic ratio 1:1 of cobalt, a lithium carbonate and cobalt hydroxide are heat-treated by 850-degreeC in air for 20 hours, an Ishikawa style stone mill mortar grinds, and it is  $LiCoO_2$  with a mean particle diameter of 5

micrometers. It obtained. Moreover, it mixes with a lithium by the atomic ratio 1.1:1 of cobalt, a lithium carbonate and cobalt hydroxide are heat-treated by 850-degreeC in air for 20 hours, an Ishikawa style stone mill mortar grinds, and it is Li1.1 CoO<sub>2</sub> with a mean particle diameter of 1 micrometer. It obtained. subsequently, LiCoO<sub>2</sub> Li1.1 CoO<sub>2</sub> the weight ratio 9:1 -- enough -- mixing -- the inside of air -- 700-degreeC -- 10 hours -- heat-treating -- a particle front face -- Li1.1 CoO<sub>2</sub> from -- becoming -- the interior of a particle -- LiCoO<sub>2</sub> from -- the multiple oxide of the becoming lithium and cobalt was obtained. this multiple oxide, the acetylene black as an electric conduction agent, and the polyvinylidene fluoride as a binder -- the weight ratio 90:6:4 -- mixing -- a positive electrode -- a mixture -- preparing -- this positive electrode -- a mixture -- moulding pressure 2 t/cm<sup>2</sup> Pressing was carried out to discoid with a diameter of 20mm, it heat-treated by 250-degreeC for 2 hours, and the positive electrode was produced.

[0021] The rolled plate of a metal lithium was pierced to discoid with a diameter of 20mm, and the negative electrode was produced.

[0022] LiClO<sub>4</sub> [ one mol / l ] (lithium perchlorate) was melted l. to the mixed solvent of the volume ratio 1:1 of propylene carbonate and 1 and 2-dimethoxyethane, and the electrolytic solution was prepared to it.

[0023] The lithium secondary battery (this invention cell) A1 of a flat form was produced using a positive electrode, an above-mentioned negative electrode, and the above-mentioned electrolytic solution (cell dimension:; with an outer diameter of 20.0mm thickness of 2.5mm). The porous membrane made from polypropylene was used for the separator.

[0024] Furthermore, the various multiple oxides shown in a table 1 were prepared like the point, these were used as positive active material, and this invention cells A2-A6 and the comparison cells B1-B11 were produced. Each used multiple oxide mixes, heat-treats and produces the multiple oxide of the lithium of 5 micrometers of mean diameters and cobalt which should constitute the interior of a particle, and the multiple oxide of the lithium of 1 micrometer of mean diameters and cobalt which should constitute a particle front face by the weight ratio 9:1. In addition, the multiple oxide of the same presentation also mixes the multiple oxide of the lithium of these two presentations and cobalt with which mean diameters differ, and a particle front face and the interior of a particle heat-treat it, and produce.

[0025] About above-mentioned this invention cells A1-A6 and comparison cells B1-B11, after charging to 4.3V by 3mA, the charge-and-discharge cycle trial which makes 1 cycle the process which discharges to 3V by 3mA was performed, and the charge-and-discharge cycle life and the maximum discharge capacity of each cell were calculated. It was estimated that a charge-and-discharge cycle life was also at the number of charge-and-discharge cycles until discharge capacity falls to 80% of the maximum discharge capacity. A result is shown in a table 1.

[0026]

[A table 1]

[0027] As shown in a table 1, this invention cells A1-A6 have a long charge-and-discharge cycle life compared with the comparison cells B1-B11. This data shows that the lithium secondary battery the lithium on the front face of a particle and the atomic ratio of cobalt excelled [ lithium secondary battery ] in the charge-and-discharge cycle property extremely by using the multiple oxide of the lithium inside a particle, a larger lithium than the atomic ratio of cobalt, and cobalt as positive active material is obtained.

[0028] (Experiment 2) In this experiment, it investigated about the effectiveness at the time of applying this invention to the lithium secondary battery which uses the multiple oxide of a lithium and nickel as positive active material.

[0029] It replaced with cobalt hydroxide and nickel hydroxide was used, and except having heat-treated in the oxygen ambient atmosphere, like the experiment 1, the multiple oxide of a mutually different lithium and nickel was produced, and the presentation inside the particle front face shown in a table 2 and/or a particle used each of these multiple oxides as positive active material, and produced this invention cells A7-A12 and the comparison cells B12-B22. Subsequently; the charge-and-discharge cycle trial of the conditions same about each cell as experiment 1 was performed, and the charge-and-discharge cycle life and the maximum discharge capacity of each cell were calculated. A result is shown in a table 2.

[0030]  
[A table 2]

[0031] As shown in a table 2, this invention cells A7-A12 have a long charge-and-discharge cycle life compared with the comparison cells B12-B22. This data shows that the lithium secondary battery the lithium on the front face of a particle and the atomic ratio of nickel excelled [ lithium secondary battery ] in the charge-and-discharge cycle property extremely by using the multiple oxide of the lithium inside a particle, a larger lithium than the atomic ratio of nickel, and nickel as positive active material is obtained.

[0032] (Experiment 3) In this experiment, it investigated about the effectiveness at the time of applying this invention to the lithium secondary battery which uses the multiple oxide of a lithium, cobalt, and nickel as positive active material.

[0033] As multiple oxide synthetic powder, like the experiment 1, the multiple oxide of a lithium, mutually different cobalt, and mutually different nickel was produced, and the presentation inside the particle front face shown in a table 3 and/or a particle used each of these multiple oxides as positive active material, and produced this invention cells A13-A18 and the comparison cells B23-B33 except having used a lithium carbonate, cobalt hydroxide, and nickel hydroxide. In addition, all the mixed mole ratios of the cobalt hydroxide at the time of producing a multiple oxide and nickel hydroxide were set to 9:1. Subsequently, the charge-and-discharge cycle trial of the conditions same about each cell as experiment 1 was performed, and the charge-and-discharge cycle life and the maximum discharge capacity of each cell were calculated. A result is shown in a table 3.

[0034]

[A table 3]

[0035] As shown in a table 3, this invention cells A13-A18 have a long charge-and-discharge cycle life compared with the comparison cells B23-B33. This data shows that the lithium secondary battery the atomic ratio with the lithium on the front face of a particle, cobalt, and nickel excelled [ lithium secondary battery ] in the charge-and-discharge cycle property extremely by using the multiple oxide of the lithium inside a particle, cobalt and a larger lithium and cobalt than an atomic ratio with nickel, and nickel as positive active material is obtained.

[0036] (Experiment 4) In this experiment, it investigated about the effectiveness at the time of applying this invention to the lithium secondary battery which uses the multiple oxide of a lithium, cobalt, nickel, and manganese as positive active material.

[0037] As multiple oxide synthetic powder, a lithium carbonate, cobalt hydroxide, nickel hydroxide, and a manganese dioxide are used, and it is made to be the same as that of experiment 1 except having heat-treated in the oxygen ambient atmosphere. The multiple oxide of a lithium, cobalt, mutually different nickel, and mutually different manganese was produced, and the presentation inside the particle front face shown in a table 4 and/or a particle used each of these multiple oxides as positive active material, and produced this invention cells A19-A24 and the comparison cells B34-B44. In addition, all the mixed mole ratios of the cobalt hydroxide at the time of producing a multiple oxide, nickel hydroxide, and a manganese dioxide were set to 1:7:2. Subsequently, the charge-and-discharge cycle trial of the conditions same about each cell as experiment 1 was performed, and the charge-and-discharge cycle life and the maximum discharge capacity of each cell were calculated. A result is shown in a table 4.

[0038]

[A table 4]

[0039] As shown in a table 4, this invention cells A19-A24 have a long charge-and-discharge cycle life compared with the comparison cells B34-B44. This data shows that the lithium secondary battery the atomic ratio with the lithium on the front face of a particle, cobalt, nickel, and manganese excelled [ lithium secondary battery ] in the charge-and-discharge cycle property extremely by using the multiple oxide of the lithium inside a particle, cobalt, nickel and a larger lithium and cobalt than an atomic ratio with manganese, and nickel, and manganese as positive active material is obtained.

[0040] Although that to which a particle front face and the interior of a particle mixed, heat-treated and produced the multiple oxide powder of this presentation which is two with which mean particle diameter differs as a multiple oxide of the same presentation was used in the above-mentioned experiments 1-4, also when mean particle diameter used the multiple oxide powder which is 5 micrometers as it was, it checked separately that the almost same result was obtained.

[0041] Although investigated in the above-mentioned experiments 1-4 about the effectiveness at the time of applying a multiple oxide with at least one sort of transition elements chosen from the group which consists this invention of a lithium, cobalt and nickel, and manganese to the lithium secondary battery used as positive active material Also about the lithium secondary battery which used other multiple oxides specified by this invention Each of lithiums on the front face of a particle of a multiple oxide, atomic ratios of a transition element, and the lithiums inside a particle and the atomic ratios of a transition element are set to 0.9-1.2, and the former atomic ratio is made larger than the latter atomic ratio. It checked separately that the lithium secondary battery which was extremely excellent in the charge-and-discharge cycle property was obtained.

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